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Concentrations and Patterns of Photochemical Oxidants in the United States

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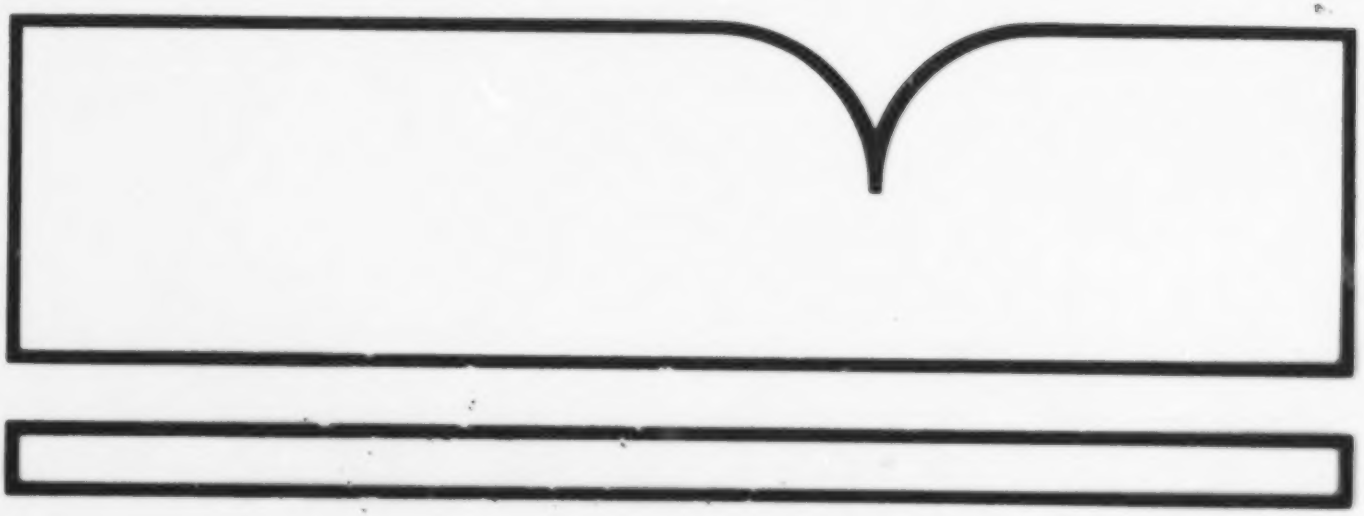

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By

B. E. Tilton[1] and S. A. Meeks[2]

EPA Project Officer
B. E. Tilton

[1]Environmental Criteria and Assessment Office
U.S. EPA, Research Triangle Park, NC 27711

[2]Atmospheric Sciences Research Laboratory
U.S. EPA, Research Triangle Park, NC 27711

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CONCENTRATIONS AND PATTERNS OF PHOTOCHEMICAL OXIDANTS IN THE UNITED STATES

B.E. Tilton[a] and S.A. Meeks[b]

Environmental Criteria and Assessment Office[a], and Atmospheric Sciences Research Laboratory[b], U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, USA

ABSTRACT

A broad overview is first given of concentrations of ozone and PAN at urban sites in the U.S. and of ozone at selected nonurban sites. Then, sample diurnal curves for ozone at suburban and nonurban sites are presented. Highest concentrations of both oxidants occur in California, where the second-highest 1-hr concentration of ozone in 1983 was 0.37 ppm and the highest PAN concentration reported in this decade was 0.047 ppm, in 1980. At selected nonurban sites, maximum 1-hr ozone levels for 1978-1981 were about half the second-highest 1-hr ozone levels at urban sites in those years. Examples presented of temporal patterns of ozone show distinct seasonality and diurnality, demonstrate some general differences in diurnality and seasonality at suburban versus nonurban sites, and point up potential implications for exposures to ozone of populations, vegetation, and other receptors. Data on co-occurrences of ozone with nitrogen dioxide or sulfur dioxide indicate relatively few such events at levels of potential concern for vegetation. Data on ozone and nitrogen dioxide at levels of possible concern for public health show even fewer instances of co-occurrence.

INTRODUCTION

Aerometric data for ozone are essential in the United States for determining compliance by individual states with the National Ambient Air Quality Standards (NAAQS) for ozone. In addition, such data are useful for other purposes, including: (1) performing comprehensive exposure assessments; (2) identifying those components of exposure dynamics that elicit observed effects, such as mean and peak concentrations, diurnality of concentrations, and respites between peak concentrations; (3) designing experiments such that the protocols, pollutant measurements, and statistical methods used will produce time-resolved data on exposure-response relationships; and (4) formulating the best exposure statistic(s) for NAAQS for the protection of public health and welfare.

Through examples, descriptive information is given here on some geographic and temporal patterns of ozone and PAN concentrations observed in the U.S. that have particular relevance for assessing exposures and for designing experimental protocols.

OVERVIEW OF OXIDANT CONCENTRATIONS

Nationwide frequency distributions are shown in Figure 1 for 3-yr averages of the first-, second-, and third-highest 1-hr concentrations, measured by UV or chemiluminescence, at predominantly urban monitoring stations in the U.S.

(Ref. 1). This figure also shows the highest 1-hr concentration at sites of the National Air Pollution Background Network (NAPBN), averaged for the same 3 yr. This network, established to monitor ozone concentrations in nonurban areas minimally affected by manmade sources, consisted of eight sites in National Forests in Oregon (OR), Arizona (AZ), Montana (MT), Wisconsin (WI), Missouri (MO), Louisiana (LA), North Carolina (NC), and Vermont (VT) (Ref. 2). As these data indicate, 50 percent of the second-highest 1-hr concentrations for 1979 through 1981 at the urban stations were $\leq$0.12 ppm, the level of the current U.S. NAAQS for ozone. Second-highest 1-hr ozone concentrations at the eight NAPBN sites were about two-thirds the urban concentrations at the 50th percentile but only about two-fifths the urban levels at the 95th percentile. The data for urban areas, it should be noted, are heavily influenced by data from California because of the disproportionately large number of monitoring stations and the greater frequency of occurrence of high ozone concentrations in California (Ref. 1).

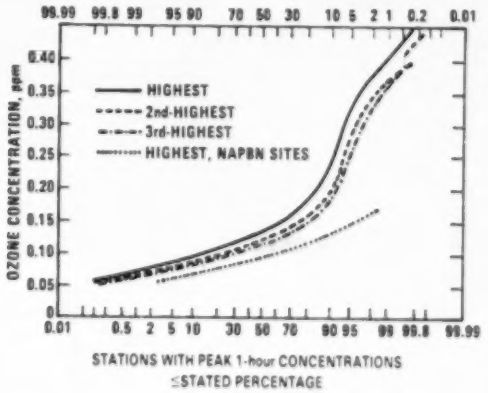

Figure 1. Distributions of the three highest 1-hour ozone concentrations at valid sites (906 station-years) aggregated for 3 years (1979, 1980, and 1981) and the highest ozone concentrations at NPABN sites aggregated for the same years (24 station-years) (Refs. 1,2).

Figure 2 shows ozone data for 1983 for respective geographic regions of the U.S. (Refs. 1, 3). Shown here for each region are the population (in thousands), number of standard metropolitan statistical areas (SMSAs) in the region that have populations $\geq$0.5 million, the average of the 1983 second-highest 1-hr ozone concentrations for those SMSAs, and the range of the 1983 second-highest value among the SMSAs. (The second-highest 1-hr value for a given site and year is determined from a validated data set consisting of all 1-hr daily maxima in that year at that site. Here the second-highest 1-hr values for the

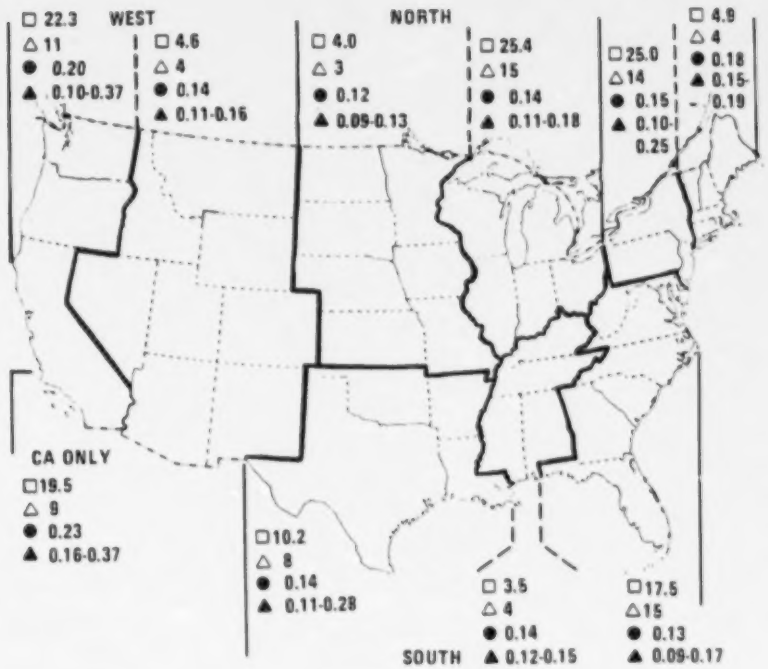

Figure 2. Average and range of second-highest 1-hour daily maximum ozone concentrations for 1983 for geographic regions of the U.S., derived from data for SMSAs with populations ≥0.5 million (Key: □ population, millions; △ no. of SMSAs in regions with population ≥0.5 million; ● average of second-highest 1-hour daily maxima; ▲ range of second-highest 1-hour daily maxima.)

year at all sites in the SMSAs have been used to derive SMSA averages and ranges.) As shown, in 1983 the highest 1-hr ozone concentrations (i.e., the second-highest 1-hr values) occurred on the Pacific coast, especially in California; in the northeast (New England and Middle Atlantic states); around the Great Lakes (East North Central states); and in the Gulf Coast area (West South Central states). For each of these areas, the causes of elevated pollution levels are unique, complex, and interactive, such that meteorology and population-related factors combine to produce the regional concentrations shown here.

No air quality standard for peroxyacetyl nitrate (PAN) exists in the U.S. and PAN is therefore not monitored routinely. Available data all come from special field investigations, and thus are sparse as well as not very comparable, since sampling intervals, time of day, and even seasons have differed among studies. Data from the more comparable studies in urban and suburban areas, however, are briefly summarized in Table 1 (Refs. 1, 4-14).

TABLE 1.
Summary of PAN concentrations in urban areas of the United States[a]

Urban area	Sampling period	Concn., ppb Avg.	Max.	Ref.
Riverside, CA	1980[b]	4.9	41.6	(4)
Claremont, CA	1980; Sept., Oct.[c]	13	47	(5)
Riverside, CA	1977; Apr., May[c]	1.6	5.7	(6)
Riverside, CA	1977; Jul., Aug., Oct.[b]	7	18	(7)
Riverside, CA	1975-76; May-Oct.[c]	3.6	32	(8)
West Covina, CA	1977; Aug., Sept.[c]	9	20	(9)
Riverside, CA	1967-68; Aug.-Apr.[c]	4.6	58	(10)
Los Angeles, CA	1965; Sept.-Oct.[d]	31	214	(11)
Houston, TX	1976; Jul.[c]	0.4	11.5	(12)
Dayton, OH	1974; Jul., Aug.[c]	0.7	10	(13)
St. Louis, MO	1973; Jun.-Aug.[c]	1.8	19	(13)
New Brunswick, NJ	1978-80[c]	0.5	10.6	(14)

[a]Only studies with a minimum of 10 days of sampling.
[b]12 hr/day, daytime.
[c]24 hr/day.
[d]5 hr/day, 0800-1300.

Data on PAN in nonurban areas of the U.S., limited to studies done in the 1970s, indicate that nonurban concentrations of PAN overlap those found at urban locations outside California. At remote nonurban locations, PAN concentrations are generally somewhat lower still, with average concentrations on the order of about 0.1 to 0.6 ppb (Ref. 15).

TEMPORAL PATTERNS OF OZONE CONCENTRATIONS

The common features of the occurrence of ozone in ambient air in the U.S. have been well-documented in the open literature and have also been reviewed at length in a relatively recent publication of the U.S. Environmental Protection Agency (Ref. 1). Among the more commonly recognized characteristics of ozone in ambient air are its temporal and spatial patterns, which are such that higher concentrations of ozone occur in the U.S.: (1) in mid-spring through mid-fall; (2) in mid- to late afternoon; (3) at higher elevations, if mean concentrations are the indices used; (4) outdoors, rather than indoors; and (5) if short-term peak concentrations are the indices used, in urban versus nonurban areas (Ref. 1).

Examples are given subsequently of some temporal patterns in ozone concentrations typically observed in the U.S. The obvious should be emphasized, however; that is, for each generalized example many exceptions can be found, especially in an area as large and topographically and meteorologically diverse as the U.S.

The seasonality of distributions of 1-hr ozone concentrations is shown in Figure 3 for five urban sites and one suburban site (Morris County, NJ) in

various geographic areas of the U.S. Although the distributions vary somewhat with locality, as they would with year as well, a seasonal trend is obvious, especially in the maximum 1-hr values for each month. Note that the monthly means do not differ widely among sites, in contrast to the 1-hr maxima for each month.

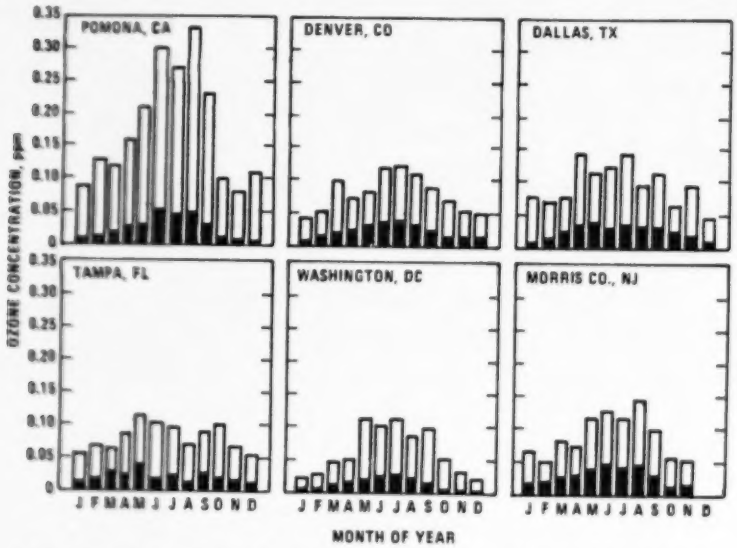

Figure 3. Seasonal distributions of ozone concentrations as indicated by monthly averages (■) and the 1-hour maximum (□) in each month at selected urban and suburban sites, 1981 (Ref. 1).

Seasonal distributions for six NAPBN nonurban sites and for Whiteface Mountain, NY, are shown in Figure 4 (Ref. 16). Note that both peak and mean concentrations are highest in spring at most of these sites. Note also the similarities in seasonal distributions of average 1-hr maxima at NAPBN sites in Oregon and Montana. These two NAPBN sites are located, respectively, at latitudes of 44°13' and 45°14' and at elevations of 1250 and 1350 m. These sites and the one in Missouri also show a pattern of elevated ozone in late summer or early fall.

Average diurnal curves for respective quarters of the year offer a succinct demonstration of both the seasonality and diurnality of ozone concentrations. Figure 5 (Refs. 2, 17, 18) shows average quarterly diurnal curves for sites in different parts of the country: (A) and (C) NAPBN sites (Ref. 2); (B) a suburban site in a city in the Los Angeles basin, Azusa, CA, which had the maximum second-highest daily 1-hr concentration in the U.S. in 1985 (Ref. 18), and (D) a suburban site in a small city, Lancaster, PA, which is situated in a

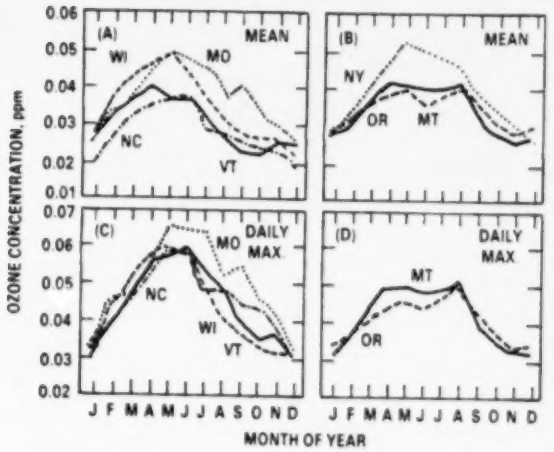

Figure 4. Seasonal distributions of ozone at nonurban sites of the NAPBN and at Whiteface Mountain, NY: (A) means of all daily 1-hour values at sites in Wisconsin (WI), Missouri (MO), Vermont (VT), North Carolina (NC), Oregon (OR), and Montana (MT) and (B) in New York (NY); (C) means of daily 1-hour maxima in each month for sites in MO, NC, WI, and VT; and (D) in MT and OR.

farming region in the northeast U.S. and which had no concentrations $\geq$0.12 ppm in 1985 (Ref. 18).

Diurnal curves for the NAPBN sites in Figure 5(A) are composite curves derived from diurnal data from 1979 for all six sites. Figure 5(C) presents quarterly diurnal distributions at a separate NAPBN site located in the Apache Sitgraves National Forest, AZ, at 33°45' latitude and an elevation of 2500 m (Ref. 17). The quarterly diurnal distributions of data from the six NAPBN sites are not unlike those from many nonurban sites and some of the suburban sites monitored in the U.S. (Ref. 1). Peak-to-mean ratios at the Arizona site, however, were close to 1.0 each quarter. Peak-to-mean ratios at the other six NAPBN sites (using composited data and the average of all daily 1-hr O_3 maxima as the peak) were 1.2, 1.2, 1.3, and 1.3, respectively, for Q1 through Q4 (see Ref. 2).

The NAPBN sites at which the data shown in Figure 5(A) were obtained are known to be affected by ozone generated from manmade emissions of precursors (Ref. 2), as determined from trajectory analyses and from forward stepwise regression analyses of ozone concentrations versus meteorological variables such as temperature (T) and relative humidity (RH); T and RH are indicative of oxidant-forming potential of local versus transported air masses. Note, however, the relatively high concentrations in the evening, nighttime, and early morning hours. These are typical of concentrations in nonurban areas, where surface deposition rather than NO scavenging appears to be the chief

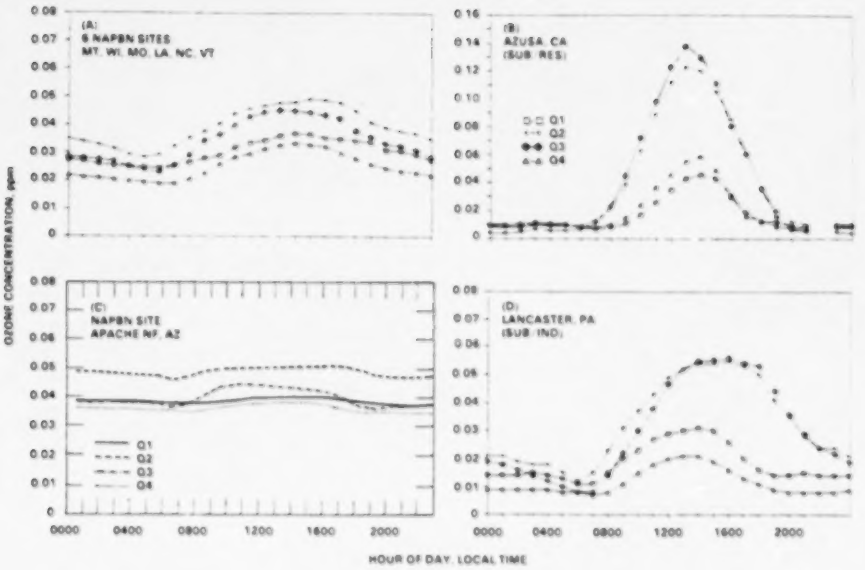

Figure 5. Quarterly diurnal curves for ozone at nonurban and suburban sites: (A) composite quarterly distributions (1979) for six NAPBN sites in MT, WI, MO, LA, NC, and VT; (C) quarterly distributions (1979) at a remote, high-elevation (2500 m MSL) NAPBN site in Arizona (AZ); (B) and (D) quarterly distributions (1985) at suburban/residental site in Azusa, CA (South Coast Air Basin) and at suburban/industrial site in Lancaster, PA (small city in farming area of northeast) (Refs. 2, 17, 18).

removal mechanism. Note the occurrence in the second and third quarters (smog season) of rather broad peaks persisting through much of the afternoon at the six NAPBN sites. The second- and third-quarter curves for Azusa, CA, on the other hand (Figure 5B), show the more typical pattern--sharper peaks occurring closer to midday--for a source area in which the ozone measured is generated locally or transported from nearby, or both. The quarterly diurnal curves from the site at Lancaster, PA (Figure 5D), show fairly broad plateaus from the morning through late evening in the smog season (Q1 and Q2), but the curves have characteristics that make them intermediate between the NAPBN and the Azusa curves. These are: (1) lower post-midnight concentrations than those at NAPBN sites; (2) greater inflection around 6:00 to 8:00 a.m. than seen in data from NAPBN sites; and (3) lower afternoon but higher evening concentrations than those at Azusa. In urban and suburban areas, ozone concentrations during the evening, nighttime, and early morning hours are usually minimal, often approaching zero (Ref. 1). Thus, ozone concentrations in some of these areas can fluctuate widely within a day, especially in the second and third quarters, as exemplified by the Azusa curves in Figure 5(B).

Questions remain in the health and vegetation literature as to the relative importance of the respective components of the dynamic nature of ozone in ambient air. For example, do short-term peak excursions above given levels induce more severe effects than static, low-level ozone concentrations; or are cumulative doses the most important aspect of exposure to ozone? In Table 2, therefore, examples of several simple measures of ozone air quality are given for the diurnal curves presented in Figure 5. The quarterly means for ozone concentrations at Lancaster and Azusa have been calculated for 24 hr and for 14 hr, the latter being the peak daylight hours from 6:00 a.m. to 8:00 p.m. Data were not available for calculating daylight means for the composite NAPBN sites or the NAPBN site in Arizona. Data for daylight hours are important for assessing population exposures, since most people who are outdoors for any appreciable length of time are there in daylight; and since vegetation, though exposed 24 hr/day, is affected during the hours when plant stomates are open and gas exchange and photosynthesis are occurring.

For the 14-hr daylight period, annual cumulative ozone at Lancaster in 1985 was 63 percent of that at Azusa and second- and third-quarter cumulative ozone at Lancaster was 60 percent of that at Azusa. The second-highest 1-hr ozone concentration at Lancaster for the year, however, was only 32 percent of the same measure at Azusa.

TABLE 2.
Summary ozone statistics for sites in Figure 5 (ppm)

	Lancaster, PA		Azusa, CA		"Background site"[a]	Apache NF, AZ
	24-hr	14-hr[b]	24-hr	14-hr	24-hr	24-hr
Quarter	Avg. O_3 concn./quarter,ppm					
Q1[c]	0.018	0.022	0.017	0.023	0.030	0.039
Q2	0.033	0.041	0.043	0.064	0.040	0.049
Q3	0.031	0.038	0.044	0.068	0.034	0.040
Q4	0.012	0.014	0.020	0.027	0.025	0.037
Annual	0.024	0.029	0.031	0.046	0.032	0.041
Second-highest 1-hr O_3 in yr	0.114		0.360		0.125	NA[d]
Cumulative O_3/yr						
Q2 + Q3	140	101	192	169	162	195
Annual	210	148	272	235	280	361

[a]Treats the six NAPBN sites as one hypothetical site for monitoring continental background O_3 at ground level.
[b]Daylight hours, 6:00 a.m. through 7:00 p.m.
[c]Q1 = January-March; Q2 = April-June; Q3 = July-September; Q4 = October-December.
[d]Data not available.

If one uses the quarterly mean concentrations found from the composite NAPBN data to represent one hypothetical site (nonurban area), the total ozone to which a receptor could theoretically be exposed in a year at such a site would be ca. 280 ppm (i.e., exposed 24 hr/day, 365 days/yr). As difficult as it may be to grasp, the cumulative 1-yr ozone concentration is somewhat greater at the hypothetical "background site" and one and one half times greater at the high-elevation NAPBN site in Arizona--where quarterly mean ozone concentrations range from about the lower to the upper bounds of estimated U.S. continental background ozone (Ref. 1)--than at the Azusa, CA, site where the second-highest daily 1-hr level for 1985 was 0.360 ppm, the highest such value measured in the whole nation in 1985. Comparison of the possible cumulative exposures at these sites during the second and third quarters, however, reveals that about 70 percent of the cumulative ozone for the year occurs in those quarters at Azusa but only 58 percent at the hypothetical "background site." Thus, the cumulative ozone differs little between Azusa and the hypothetical site, but the "dose rates" of the potential exposures of biological receptors at the two sites differ somewhat more substantially.

These very simple statistics reinforce the necessity for obtaining additional concentration-response data for health and vegetation effects, especially data on concentration times time relationships (C x T). Further inquiries are needed, for example, into the differences in observed effects that occur with exposures to low-level, steady-state concentrations versus intermittent, episodic concentrations, as well as into the effects of cumulative exposures generally and specifically the effects from cumulative ozone exposures accruing at varying dose rates.

The quarterly diurnal curves presented here mask the day-to-day variations that can occur at the same monitoring site. Figure 6 shows true diurnal curves (single-day curves) at the Azusa, CA, site and at a residential/rural site in San Bernardino, CA, about 35 to 40 miles southeast of Azusa but also within the Los Angeles air basin. Note especially the diversity of the patterns for the 3 successive days at Azusa. The time of the respective peak 1-hr concentrations shifted from 1:00 p.m. (1300) on August 24 to 3:00 p.m. (1500) on August 25. The 1-hr peak concentrations were 0.36 ppm on August 24, 0.22 ppm on August 25, and 0.09 ppm on August 26. The 24-hr means for those 3 days were 0.089, 0.082, and 0.026 ppm, respectively. Peak-to-mean ratios for those 3 days were, respectively, 4.04, 2.68, and 3.46.

Comparison of the diurnal curves from the two sites is of note partly to point out the elevated O_3 concentrations during the evening, night, and early morning hours at the San Bernardino site (at midnight, 0.04 ppm on June 18 and 0.08 ppm on June 13), a pattern similar to that seen in the NAPBN data. Peak-to-mean ratios for these 2 days at the San Bernardino site are

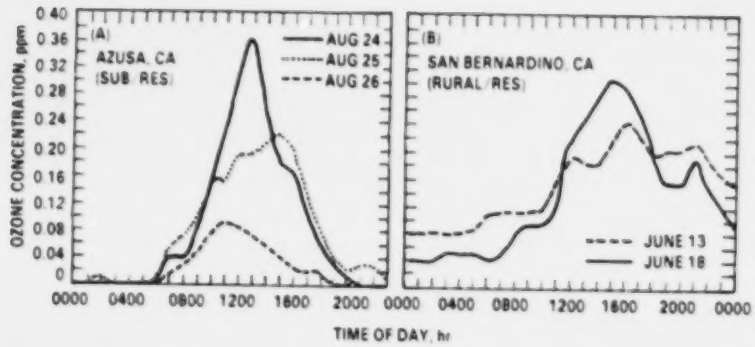

Figure 6 (A) Diurnal curves for 3 successive days, Azusa, CA, August 24-26, 1985; (B) diurnal curves at San Bernardino, CA, for day with the maximum 1-hour value for the year (June 18, 1985) and day with the maximum 1-day mean for the year (June 13, 1985) (Ref. 18).

lower than those at the Azusa site: 1.62 for June 13 (0.240/0.148 ppm) and 2.22 for June 18 (0.300/0.135 ppm). Nevertheless, cumulative ozone, both for the days depicted here and for the year, is much greater at the San Bernardino site: 272 ppm ozone per year for Azusa versus 464 ppm per year for San Bernardino. In passing it should be noted that the San Bernardino site reflects potential exposures of the mixed-conifer forest in the San Bernardino Mountains, since air parcels monitored at this site often pass into the mountain range (Ref. 1). The San Bernardino forest has been documented as showing ozone-induced damage (Ref. 1 and references therein).

Ozone is commonly perceived to be a regional pollutant, but concentrations can differ markedly in spatial distribution, as the differences in diurnal distributions shown for these two sites in the same airshed would suggest. Such differences in spatial distributions can result in fairly substantial gradients and differences in potential exposures to ozone within the same airshed or even the same city. Downwind of well-mixed urban plumes, concentrations in a city or area can be relatively homogeneous; but in a large metropolis, appreciable gradients in ozone concentrations can exist from one side of the city to the other (Ref. 1). Recent data, for the Los Angeles megalopolis are shown in Figure 7 for five sites including the Azusa and San Bernardino sites already discussed. As Figure 7 shows, the number of episode days (i.e., days when ozone concentrations were $\geq$0.20 ppm) varied widely among sites within, east, and southeast of Los Angeles (LA) in the years shown (Ref. 19). Some of these cities in the Los Angeles area are within daily commuting distance of each other. Thus, such differences in potential exposures to ozone should be taken into consideration, where possible, in exposure assessments.

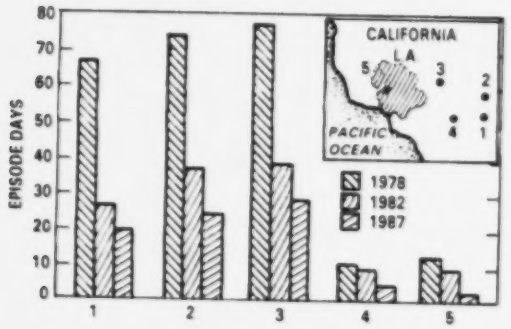

Figure 7. Comparison of ozone episodes (≥0.2 ppm) at selected monitoring stations in the California South Coast Air Basin (1-Riverside; 2-San Bernardino; 3-Azusa; 4-Anaheim; 5-downtown Los Angeles (Ref. 19).

One final point may be of interest with respect to ozone: that is, the extent of its co-occurrence with other major gas-phase pollutants such as NO_2 and SO_2, both of which have been shown to be respiratory irritants and to be injurious to vegetation if present at toxic levels.

The diurnal curves shown earlier for ozone in urban areas would indicate, if they are typical, that the likelihood of the co-occurrence of ozone with NO_2 in short-term peaks at levels of concern should be minimal, since NO_2 concentrations peak twice per day, in morning and evening (Ref. 1). Where diurnal patterns are flatter--as in many nonurban or smaller urban areas--the likelihood of simultaneous co-occurrence of ozone and NO_2 is greater but at lower concentrations of both. Since about 95 percent of manmade emissions of SO_2 come from stationary sources, diurnal patterns are less clearcut and thus co-occurrences of SO_2 with ozone, NO_2, or both, may possibly be more frequent.

Lefohn and Tingey (Ref. 20) examined data for rural or other agriculturally important sites for May through September 1981, from three aerometric monitoring networks in the U.S. (SAROAD, EPRI-SURE, TVA; see Ref. 20), to determine whether O_3 co-occurs with SO_2 and NO_2. They selected a concentration cutoff of $\geq$0.05 ppm (1-hr average) and simultaneous occurrence within the same hour as the criteria for defining co-occurrences. The concentration cutoff was based on reports showing effects on vegetation of 2 ppm NO_2 plus 0.05 ppm SO_2 and 0.05 ppm O_3 plus 0.05 ppm SO_2 (see Ref. 20). Data from all types of sites (e.g., urban, rural, point source-related) were examined to ensure lack of bias by type of location. Their analysis showed that co-occurrences in the U.S. of SO_2-O_3, NO_2-O_3, or SO_2-NO_2 pollutant pairs are short-lived (hours), widely separated in time (weeks, sometimes months), and that periods of co-occurrence represent a very small portion of the growing

periods of agricultural crop species. Figure 8 (Ref. 20) shows the frequency distribution of O_3-SO_2 and O_3-NO_2 co-occurrences by number of sites and number (1-hr each) of co-occurrences. Data are similar for the two pollutant pairs

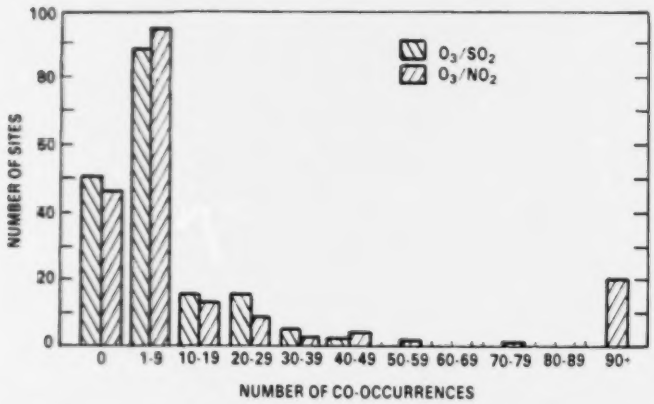

Figure 8. Frequency distribution of co-occurrence of ozone with nitrogen dioxide or sulfur dioxide. Co-occurrence is defined as the simultaneous occurrence of 1-hour concentrations of ≥0.05 ppm ozone and either ≥0.05 ppm nitrogen dioxide or ≥0.05 ppm sulfur dioxide. Data are from 176 site-years of ozone-sulfur dioxide co-monitoring and 194 site-years of ozone-nitrogen dioxide co-monitoring (Ref. 20).

except for the upper end of the distribution for O_3 plus NO_2. This upper end of the range represents high-NO_2 rural/agricultural sites and may represent high-O_3 sites as well, since in lower-O_3 and lower-NO_2 areas the two diurnal curves would most likely overlap at levels lower than the concentration cutoffs chosen.

In subsequent work, Lefohn et al. (Ref. 21) expanded their definition of co-occurrences to include the occurrence within the same 24-hr period of pollutant pairs (among SO_2, NO_2, O_3) at concentrations of $\geq$0.03 ppm and $\geq$0.05 ppm. They also included data on additional rural/agricultural sites (Ref. 21). Results confirmed the earlier analysis (Ref. 20), i.e., SO_2 and NO_2 at 1-hr concentrations each of $\geq$0.03 and O_3 at $\geq$0.05 ppm occur infrequently, either singly or in combination, at rural-agricultural sites. These findings are consistent with the analysis of Jacobson and McManus (Ref. 22), who found that simultaneous (same-hour) co-occurrences of SO_2 and NO_x were infrequent in the Ohio River Valley, even in an area that contains four coal-fired power plants.

Data from population-oriented monitoring sites (mainly center-city and suburban) were subsequently examined (Ref. 23) to determine whether O_3 co-occurs with NO_2 at those sites at concentrations of potential concern for

public health. Co-occurrences were defined as the occurrence of both pollutants within the same 24-hr period at 1-hr average concentrations of 0.12 ppm O_3 and 0.3 ppm NO_2. These concentrations were selected on the basis of suggested or demonstrated health effects at levels of $\geq$0.12 ppm O_3 for 2 hr (e.g., Ref. 24) and at levels of $\geq$0.3 to $\geq$0.5 ppm NO_2 for $\leq$1 hr (e.g., Ref. 25). Analyses were done on 4787 site-years of O_3 data and 2141 site-years of NO_2 data for April through October, 1978 through 1984. Multiple years of data from the same site were treated as independent data sets in the analysis. Episodic levels of both pollutants occurred during these years at urban sites in at least eight states, but co-occurrences in the same-hour, same 24 hr, or both were found only in data from monitoring stations in southern California. There, 1-hr NO_2 concentrations $\geq$0.3 ppm preceded, followed, or accompanied 1-hr O_3 concentrations $\geq$0.12 ppm a total of 23 times in 3 yr (1979-1981) among 15 separate sites. NO_2 and O_3 occurred together in the same hour at the specified concentrations only 6 of the 23 times. Thus, the data indicate the infrequent co-occurrence of 1-hr concentrations of O_3 and NO_2 at levels of possible concern for health. Co-occurrences of O_3 and NO_2 at urban sites at lower levels for multiple hours are a subject for further investigation, as are the possible co-occurrences of O_3 plus SO_2 at levels of potential concern.

Figure 9 shows an example of diurnal curves for O_3, SO_2, and NO_2 derived from 1-hr measurements made on the same day at a site in Fontana, CA (Ref. 20), a high-NO_2, high-O_3 site. These curves, along with the data of Lefohn et al. (Ref. 23) on co-occurrences of O_3 plus NO_2, suggest the relevance of health

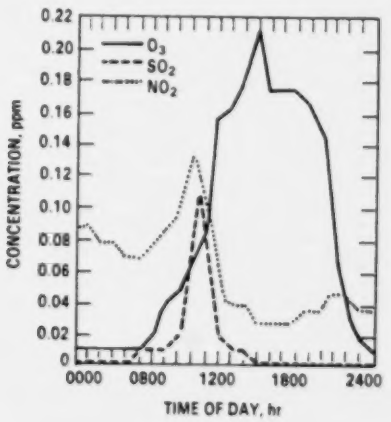

Figure 9. Example of diurnal curves of ozone, sulfur dioxide, and nitrogen dioxide on the same day at Fontana, CA (Ref. 20).

effects research involving sequential exposures to O_3 plus NO_2 or SO_2 and simultaneous exposures to NO_2 plus SO_2. The latter might be especially relevant, for example, in the study of responses of mild asthmatics.

TEMPORAL PATTERNS IN PAN CONCENTRATIONS

The more common features of peroxyacetyl nitrate (PAN) behavior in ambient air in the U.S. have been identified but are less well-documented than for ozone because of the paucity of data on PAN. The distributions of PAN concentrations in ambient air may be concisely summarized by saying that they qualitatively resemble those of ozone (Refs. 1, 15).

Two examples are presented here of the temporal distributions of PAN in ambient air in the U.S. Figure 10 (derived from Ref. 5) shows the seasonal distributions of PAN concentrations from August through April, 1967-1968 and 1980. Distributions were not shown by Temple and Taylor (Ref. 4) for May through July, which are known to be high-oxidant months in Riverside, CA. Other data presented (below and Table 2) indicate, however, that higher average concentrations of PAN are seen in the late spring and summer months, with the occurrence of the lowest average PAN concentrations but some of the higher maxima in winter, as is evident from this graph.

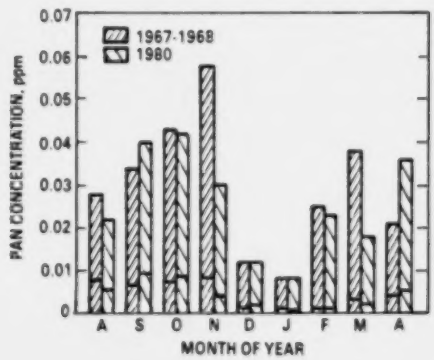

Figure 10. Seasonal distribution of daylight average and maximum PAN concentrations at Riverside, CA, 1967-1968 and 1980 (Ref. 4).

An intensive study of photochemical air quality in the South Coast Air Basin of California was conducted in summer 1987. Among the pollutants measured were ozone, nitrogen dioxide, volatile organic compounds, PAN and various other trace nitrogenous species, sulfur dioxide, total sulfate, and total nitrate. Preliminary data are reported here for the observed concentrations and patterns of PAN and other trace nitrogenous species.

Measurements of PAN were made each 15 min for 24 hr/day at Claremont, CA, for most of the June 9 through September 3 study. PAN was measured by GC-ECD (Ref. 26) and measurements were calibrated by IR spectrophotometry (PAN synthesis, Ref. 27; PAN quantification by IR, Ref. 28). Results for the PAN measurements from the total study period are given in Table 3.

TABLE 3.
PAN concentrations at Claremont, CA, June 9 through September 3, 1987

	June	Jul.	Aug.-Sept.	Total period
Concn., ppb				
Maximum	25.49	19.61	23.92	25.49
Minimum	<0.01	<0.01	<0.01	<0.01
Average	4.77	2.97	3.90	3.88
Median	2.94	1.96	2.94	2.57
(No. samples)	(2021)	(2185)	(1638)	(5844)

When compared with other 24-hr/day data for the smog season in the South Coast Air Basin, these data show both maxima and means to be quite similar to values reported from the late 1960s through the 1980s (e.g., Refs. 5, 9, 10). Compared with 11 days of data from the same Claremont site in 1980 (Ref. 5), the PAN concentrations measured in 1987 were somewhat lower. Meteorological conditions in California in summer 1987 are known, however, to have been atypical, resulting both in lower PAN and lower ozone concentrations than are usually observed.

Ozone data for 6 of the most intensively monitored days of the study are shown in Table 4, along with PAN-to-ozone ratios for those days. Ozone concentrations for the 6 days ranged from $\leq$1 ppb to 286 ppb and PAN concentrations ranged for 0.6 ppb to 20.8 ppb. At night and in the early morning, PAN concentrations exceeded those of ozone; and [(PAN/O_3) x 100] ranged as high as 360 percent. In all but one instance of extremely high ratios, however, reported ozone levels were below the recommended range for the monitoring instrumentation. Thus, PAN-to-ozone ratios were calculated for Table 4 only for the 1-hr daily maximum concentration of ozone for each day. Though both PAN and ozone concentrations were lower than typical because of the atypical meteorology for the summer, the PAN-to-ozone ratios are similar to those reported by Altshuller for urban areas in California in the 1970s (Ref. 15).

The diurnal curves for O_3, PAN, HONO, HNO_3, and NH_3 for 2 days, including the day having the highest maximum PAN in the 3-month study period, are shown in Figure 11. Inorganic species were measured by annular denuder methodology

TABLE 4.
Ozone concentrations (ppb) and PAN-to-ozone ratios at Claremont, CA, July 13-15 and August 27-29, 1988

O_3 concn.; or ratio	Date 7/13	7/14	7/15	8/27	8/28	8/29	Average
24-hr average	61	60	43	64	76	80	64
14-hr average	92	94	68	101	120	122	100
24-hr cumulative	1463	1446	1043	1538	1824	1911	1494
14-hr cumulative	1383	1413	1024	1515	1796	1833	1494
Daily 1-hr maximum	215	235	147	239	286	244	228
$(PAN/O_3) \times 100$ at 1-hr O_3 maximum	6	6	5	6	8	9	7

[a] 6:00 a.m. through 8:00 p.m. readings covering 14 hours.

(Ref. 29) as modified by Vossler et al. (Ref. 30). Note the general similarities in timing and magnitude of PAN and HNO_3 peaks. In earlier work reported by Tuazon et al. (Ref. 7), PAN formation was shown to trail that of ozone somewhat and its disappearance to parallel that of HNO_3. The ozone peaks occurred at this particular site at around 3:00 to 4:00 p.m. (1500 to 1600), somewhat later than reported for ozone by Tuazon et al. for 1979 (Ref. 7).

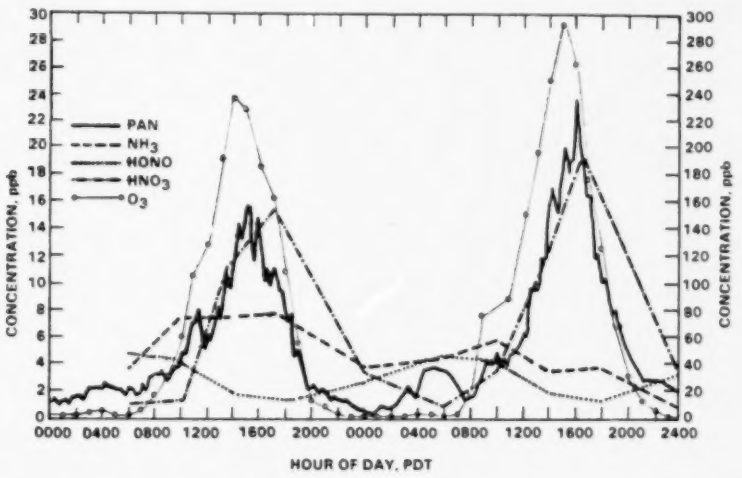

Figure 11. Diurnal curves for ozone and PAN and other trace nitrogenous compounds, August 27 and 28, 1987, Claremont, CA.

SUMMARY

A broad overview of concentrations of ozone and PAN in the U.S. has been presented. In addition, aerometric data for ozone and PAN from selected sites have been examined for patterns of interest in relation to potential exposures

of populations or vegetation. Simple statistics that often serve as indices of ozone air quality have been compared for quarterly diurnal ozone data from selected nonurban and suburban sites in the U.S. These show that higher long-term average concentrations and greater cumulative ozone exposures can occur in nonurban than in urban/suburban areas. They indicate, as well, that daily fluctuations in ozone concentrations and in dose rates in the warm-weather months are greater in urban/suburban areas than in nonurban areas. In addition, the co-occurrence of ozone with NO_2 or SO_2 has been examined and determined to be infrequent at levels of concern for vegetation. The co-occurrence of ozone with NO_2 in urban areas at 1-hr levels of concern for health effects has been shown to be even more infrequent.

REFERENCES

1. T. McMullen, E. Robinson, and B. Tilton, in Air Quality Criteria for Ozone and Other Photochemical Oxidants, Vol. II, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1986; EPA/600/8-84/020bF, Ch. 5, pp. 5-1--5-127.
2. G. Evans, P. Finkelstein, B. Martin, N. Possiel, and M. Graves, JAPCA, 33(1983)291-296.
3. U.S. Dept. of Commerce, Bur. of Census, Statistical Abstract of the United States, 103rd edn., U.S. Govt. Printing Office, Washington, DC, 1982, p. 221.
4. P.J. Temple and O.C. Taylor, Atmos. Environ. 17(1983)1583-1587.
5. D. Grosjean, Environ. Sci. Technol. 17(1983)13-19.
6. H.B. Singh, L.J. Salas, H. Shigeishi, A.J. Smith, E. Scribner, and L.A. Cavanagh, Atmospheric Distribution, Sources, and Sinks of Selected Halocarbons, Hydrocarbons, SF_6, and N_2O, U.S. Environmental Protection Agency, Research Triangle Park, NC., 1979, Rept. No. EPA-600/3-79-107.
7. E.C. Tuazon, A.M. Winer, and J.N. Pitts, Jr., Environ. Sci. Technol., 15(1981)1232-1237.
8. J.N. Pitts, Jr., and D. Grosjean, Detailed Characterization of Gaseous and Size-Resolved Particulate Pollutants at a South Coast Air Basin Smog Receptor Site, California Air Resources Board, Sacramento, CA, 1979, Rept. No. ARB-R-5-384-70-100.
9. C.W. Spicer, in J.N. Pitts, Jr, R.L. Metcalf, and A.C. Lloyd (Eds.), Advances in Environmental Science and Technology, Vol. 7, John Wiley and Sons, New York, NY, 1977, pp. 163-261.
10. O.C. Taylor, JAPCA, 19(1969)347-351.
11. H. Mayrsohn and C. Brooks, Presentation at Western Regional Meeting of the American Chemical Society, Los Angeles, CA, November 1965. (Cited in Ref. 1.)
12. H. Westberg, K. Allwine, and E. Robinson, Measurement of Light Hydrocarbons and Oxidant Transport: Houston Area 1976, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1978, Rept. No. EPA-600/3-78-662.
13. C.W. Spicer, The Fate of Nitrogen Oxides in the Atmosphere, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1976, Rept. No. EPA-600/3-76-030.
14. T.E. Lewis, E. Brennan, and W.A. Lonneman, JAPCA, 33(1983)885-887.
15. A.P. Altshuller, Atmos. Environ., 17(1983)2383-2427.
16. J.A. Logan, J. Geophys. Res., 90(1985)10463-10482.
17. G.F. Evans, The National Air Pollution Background Network, Final Project Report, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1985, p. 9.

18. AIRS, Aerometric Information Retrieval System data base, Data file for 1985, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1988; Disc, ASCII.
19. Air Quality Digest, South Coast Air Quality Management District, El Monte, CA 91731, Fall 1987.
20. A.S. Lefohn and D.T. Tingey, Atmos. Environ., 18(1984) 2521-2526.
21. A.S. Lefohn, C.E. Davis, C.K. Jones, D.T. Tingey, and W.E. Hogsett, Atmos. Environ., 21(1987)2435-2444.
22. J.S. Jacobson and J.M. McManus, Atmos. Environ., 19(1985)501-506.
23. A.S. Lefohn, L.R. McEvoy, Jr., and B. Tilton, In preparation.
24. W.F. McDonnell, D.H. Horstmann, M.J. Hazucha, E. Seal, Jr., E.D. Haak, S. Salaam, and D.E. House, J. Appl. Physiol.: Respir. Environ. Exercise Physiol., 54(1983)1345-1352.
25. M.A. Bauer, M.J. Utell, P.E. Morrow, D.M. Speers, and F.R. Gibb, Am. Rev. Respir. Dis., 129(1984)A151 (Abstr.).
26. W.A. Lonneman, J.J. Bufalini, and G.R. Namie, Environ. Sci. Technol., 16(1982)655-660.
27. B.W. Gay, R.C. Noonan, J.J. Bufalini, and P.L. Hanst, Environ. Sci. Technol., 10(1976)82-85.
28. E.R. Stephens, Anal. Chem., 36(1964)928-929 (see also E.R. Stephens, in J.N. Pitts, Jr., and R.L. Metcalf (Eds.), Advances in Environmental Sciences, Vol. 1, Wiley-Interscience, New York, NY, pp. 119-146.
29. M. Possanzini, A. Febo, and A. Liberti, Atmos. Environ., 17(1983)2605-2610.
30. T.L. Vossler, R.K. Stevens, R.J. Paur, R.E. Baumgardner, and J.P. Bell, In press.

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